

are critical for its preparation at pressures from 3 to 8 GPa is possible. This indicates a broadening of its region of stability with pressure.

We note that quenching from a  $\text{Au}_{0.77}\text{Si}_{0.23}$  melt at  $p = 3$  GPa with a cooling rate of  $600^\circ\text{K/sec}$  leads to formation of a melt whose x-ray pattern (Fig. 2) has characteristic features suggesting the presence of a phase different from that already mentioned above in a mixture with an x-ray amorphous alloy. The position of the first peak ( $2\theta = 40^\circ$ ) agrees with data on the metallic glass in this system for the composition with 25 at. % Si,  $\sin \theta/\lambda = 0.22$  [10], which was prepared with substantially higher cooling rates,  $10^6$ - $10^8$   $^\circ\text{K/sec}$  [1].

## CONCLUSIONS

Pressure lowers the critical cooling rates required for formation of metastable phases and metallic glasses in the Au—Si system. However, a broadening of the stability region of the crystalline  $\text{Au}_{0.77}\text{Si}_{0.23}$  phase on the  $T$ - $p$ - $x$  diagram substantially changes the thermodynamic and kinetic conditions for preparation of amorphous phases. Amorphous phases are not formed at higher pressure in the range of cooling rates indicated above.

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## ELECTROPHYSICAL INVESTIGATION OF THIN-LAYERED INORGANIC COATINGS

I. V. Kochugova, L. V. Nikolaeva, and N. M. Vakser

UDC 539.216.2

Miniaturization of electrotechnical devices which leads to lower volumes of materials and higher specific characteristics requires development of insulating thin-layer coatings. These should have a wide range of useful properties (pliability, heat stability, high specific resistivity, etc.). These properties should be maintained for long periods. Continuous thin glassy films in a number of cases are irreplaceable, however, they have a very substantial shortcoming: The electrical resistivity of such films at temperatures elevated to  $400$ - $600^\circ\text{C}$  falls sharply [1].

The electrical resistivity of compositions can be raised by creation of coatings based on glassy binder and highly dispersed fillers, refractory oxides of aluminum, silicon, chromium, magnesium, etc. [2]. To this end, gelatinous solutions containing 40-65% of tetraethylorthosilicate (TEOS) as the glass-forming component and aqueous salt solutions as well as solutions containing orthophosphoric acid instead of TEOS as the glass-forming component are used.

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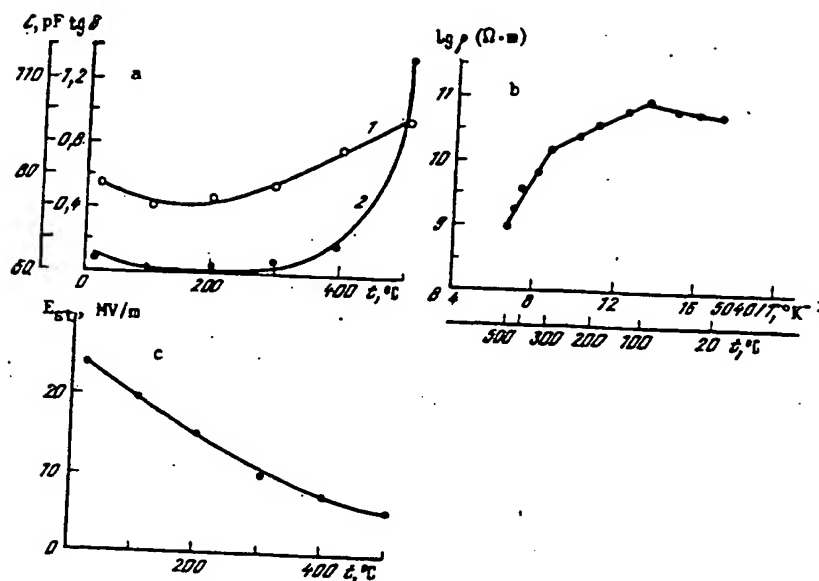


Fig. 1. Temperature dependence of  $\tan \delta$  (1) and capacitance (2) (a), specific electrical resistivity (b), and dielectric strength (c) for a sample of inorganic coating on Ni consisting of the nitrate glassy binder with  $\text{Cr}_2\text{O}_3$  filler.

Inorganic coatings (IC) which are prepared from suspensions consisting of powdered filler (50–60 mass %) distributed in a dispersing medium, a solution which forms a glassy-matrix coating upon firing, are studied. These matrices bind the filler.

The inorganic compositions were studied through the composition of the salts used (nitrates and acetates), filler ( $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ), coating thickness, firing temperature, and binding by various substrates (Al, Ni, stainless steel, and chrome).

Characteristics of the oxide powders used as filler were:  $\alpha\text{-Al}_2\text{O}_3$ , M-24 grade, content of impurities (mass %) 0.1  $\text{Fe}_2\text{O}_3$ , less than 1  $\text{SiO}_2$ , less than 0.6  $\text{Na}_2\text{O}$ , dispersivity 1–2  $\mu\text{m}$ ; and  $\text{Cr}_2\text{O}_3$ , pure grade, dispersivity, 1–3  $\mu\text{m}$ .

Dielectric characteristics were measured ( $\tan \delta$  and capacitance  $C$ ) at a frequency of 1 kHz, resistance to direct current and electrical stability in a practical frequency field between 20–500°C. In this case, standard methods and silver electrodes were used. The measurements were done on 5–10 samples of each material. Figure 1 gives the average values. The variation coefficient in all cases did not exceed 10%.

Figure 1 gives the experimental data for a coating on nickel consisting of the nitrate binder and  $\text{Cr}_2\text{O}_3$  filler. Analysis of these revealed the nature of dielectric loss and conductivity as well as the change of basic electric insulating properties with temperature change.

Lowering of  $\tan \delta$  and  $C$  between 20–150°C is related to removal of adsorbed water. Further, as the sample is fired the polarization processes are strengthened. This apparently is explained by the migration of charges accumulated at the interface of the matrix and the inclusions.

For revealing the nature of dielectric losses,  $\tan \delta$  was calculated according to an equivalent parallel scheme of dielectric replacement [3],  $\tan \delta_{\text{calc}} = 1/\omega CR$ , where  $\omega$  is the circular oscillation frequency,  $C$  is the sample capacitance,  $R$  is the direct current resistivity.

Results of the calculation showed a difference of  $\tan \delta_{\text{exp}}$  vs.  $\tan \delta_{\text{calc}}$  over the whole temperature range. Apparently, the increased losses with temperature are explained both by conductivity and by polarization.

The temperature dependence of  $\lg \rho$  is a straight line with breaks, i.e., the electrical resistivity depends on temperature by a stepped law. The portion of elevated resistivity with heating from 20 to 100°C is related to the removal of adsorbed water. The values of activation energy of conductivity between 100–300°C and higher are 0.1–1.0–1.1 eV, respectively.

Electrical stability falls smoothly as the temperature is increased.

The main parameters which affect the properties of the inorganic coating were ascertained for optimization of composition (Fig. 2).

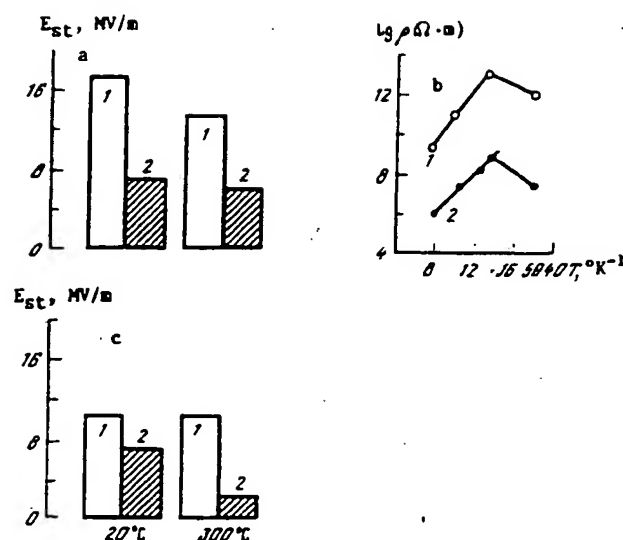


Fig. 2. Dielectric strength of coatings based on nitrate (1) and acetate (2) glassy binders at 20 and 300°C (a), temperature dependences  $\rho$  of coatings filled with corundum (1) and  $Cr_2O_3$  (2) (b), and dielectric strength of coatings on Ni (1) and stainless steel (2) at 20 and 300°C (c).

The use of corundum as filler is seen to increase the electrical resistivity over a wide temperature range. It is axiomatic that the acetates have a lower level of  $E_{st}$  by comparison to the nitrate glassy binders. The reason for this lowering of electrophysical properties of the acetate compositions is the decomposition of the acetate anion into volatile components at 400-500°C. In this case, the possible appearance of impurities of highly dispersed carbon in the composition is not excluded. Oxidation of this prevents the formation of an amorphous glass film on the surface.

The electrical resistivity increases with increased firing temperature: it is  $4.3 \cdot 10^{10}$  and  $1 \cdot 10^7 \Omega \cdot m$  for the nitrate coating on nickel with corundum filler at 20 and 300°C after firing at 400°C, and  $1.3 \cdot 10^{14}$  and  $1 \cdot 10^9 \Omega \cdot m$  after firing at 500°C.

An increase of the coating thickness on one hand improves the electrical properties due to a decreased probability of entrance of permeable defects. On the other, the elasticity and pliability of the coating is decreased.

The properties of the coatings depend on the substrate material since the product of interaction of the oxide layer and the inorganic binder is a part of the coating.

It should be noted that the most effective glassy solutions can be used for preparation of thin-layered insulator on pliable conductors. The glassy binder in the ceramic layer is formed directly on the coated surface. The coating process on the pliable conductor is done continuously and is fixed by firing at 500-700°C.

### CONCLUSIONS

Inorganic coatings placed on a metal base as a thin layer (20-25  $\mu m$ ) combine good electrical insulating properties with pliability and elasticity.

The dielectric losses in the compositions studied are defined by conductivity and polarization. They grow with heating.

The properties of the coatings, prepared from a suspension of filler in a glass-forming solution, depend mainly on the nature of filler and can change substantially with exchange of one filler by another.

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